ADSORPTION OF WATER-BORNE PB^{2+} OVER CHEMICALLY-TREATED LEAVES OF *TRIDAX PROCUMBENS*

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ABSTRACT

Lead concentrations were estimated in different components of the irrigation area, specifically the water and submerged plants (*Echinocloa colona, Cyperus rotundus, Phylantus amarus, Typha and Water hyacinth*). Unacceptable levels of Pb^{2+} were present in the irrigation water which is presumably led to considerable concentration in the submerged plants. Among the submerged plants studied, *Typha* contained the highest Pb^{2+} concentration. The adsorptive capacity of leaf powder of *Tridax procumbens* for the removal of Pb^{+2} has been demonstrated using synthetic solutions. The adsorption proceeded by pseudo second order rate scheme with rate constant standing at 61.89 g/ mg min.

***Keywords**:* lead, irrigation water, heavy metal, Thomas dam

INTRODUCTION

The birth and growth of industrial revolution has given rise to increasing environmental problems amongst which heavy metal contamination of water by industrial activities has continually registered intensive interest (Zareini *et al.,* 2005; Rawat *et al.,* 2009). The addition of heavy metal contaminated water to soil may lead to accumulation of the contaminants in the soil and subsequent uptake by plants (Smith *et al.,* 1996). Therefore, long-term irrigation using contaminated would result in adverse effects on the soil and may pose health risk where edible plants are grown (Chary *et al.,* 2008). Among heavy metals, lead has particularly been an old subject of concern to both public and policy makers. Lead is among the two most important heavy metals affecting vegetable crops (Kachenco *et al.,* 2006). The ready uptake of Pb^{2+} has been demonstrated using several submerged plants (Everard and Denny, 1985). Subsequently, other workers demonstrated the potential of submerged plants to remove this heavy metal from contaminated (Keskinkan *et al.,* 2005). However, in many cases these plants are invariably present in contaminated waters but there has been no assessment of the levels of accumulation of the heavy metals present in them.

Over the decades, there has been vigorous irrigation activity in Kano State in order to satisfy the need of the most populated Nigerian city for farm produce. We have previously shown the deleterious effect of irrigation in one of the small holder farmland sites of Kano State (Gaya and Audu, 2005). Even though heavy metal levels have been assessed in plants grown on irrigated soils, their submerged counterparts have usually been ignored. There hardly exist any report of the presence of intolerable heavy metal levels in Thomas dam and hence the present paper emphasizes on the assessment of lead levels in this area and demonstrates the possibility of its removal from water using local weed existing in the nearby communities.

MATERIALS AND METHODS

High purity chemicals ($\geq$ 98 %) were used in this study. These include CH_3COOH (Glacial), KCl, NaCl and $CaCO_3$. Other chemicals used include NaOH (97 %), HNO_3 (69 %), HCl (37 %) and NH_4OH (25 %). Lead solutions were prepared as Pb^{2+} ions from $Pb(NO_3)_2 .6H_2O$ (99 % purity) supplied by Kem Light Laboratories. Unless stated, deionised water was used in the preparation of solutions. All experiments were run in replicates and deviations were recorded as standard deviation.

Sampling

The sampling of water (2 L), was carried out in five different locations of Thomas dam at 10 cm depth, using bottle sampling method. The sampling depth was marked on a string that is tied both to the mouth of the bottle and to the bottle cap. The string can be pulled from one side of the loop to open the cap and fill up the bottle. All samples were collected during the beginning of dry season. Samples of submerged plant A-E (*Phylantus amarus, Cyperus rotundus, Water hyacinth, Echinocloa colona* and *Typha)* were collected from different locations of the Thomas dam water. The map of the dam showing sampling points (for submerged plants and irrigation water) is shown in Fig. 1 while the images of two of the submerged plants studied are in Fig. 2. The samples were oven-dried for at 70 °C for 24 hours. The dried samples of each submerged plant were ground and then mixed homogeneously by repeated coning and quartering.

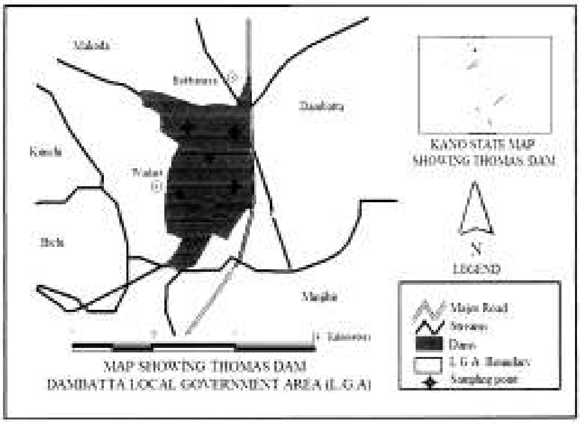

Fig. 1. *Map of Thomas dam showing sampling points of water and submerged.*
Source: GIS laboratory, Geography Department, Bayero University Kano

The leaf of *Tridax procumbens* was evaluated for efficacy of Pb^{2+} biosorption. The leaves of *Tridax procumbens* were collected from Rijiyar Zaki part of Gwale Local Government Area, Kano State and identified by a Botanist at the Department of Biological Sciences, Bayero University Kano. The leaves were shredded into smaller bits, dried in air then washed with distilled water to remove dirt and finally dried at 80 °C for 24 hours. The oven-dried leaves were ground and sieved to obtain micrometer powder particles. The leaf powder was decolourised by the procedures of Hanafiah *et al.* (2006) as follows. 20 g of each leaf powder was mixed with 200 ml NaOH (0.1 mol/L) and heated to 120 °C with occasional stirring for 30 min, followed by filtration using Whatman No. 42 filter paper. The advantages of this chemical treatment as regards to the amount of the amount of heavy metal adsorbed have been previously highlighted (Ngah, 2008). The residue left after filtration was washed until the filtrate pH was 7. The latter was dried at 50 °C overnight and used as biosorbent for Pb^{2+} removal.

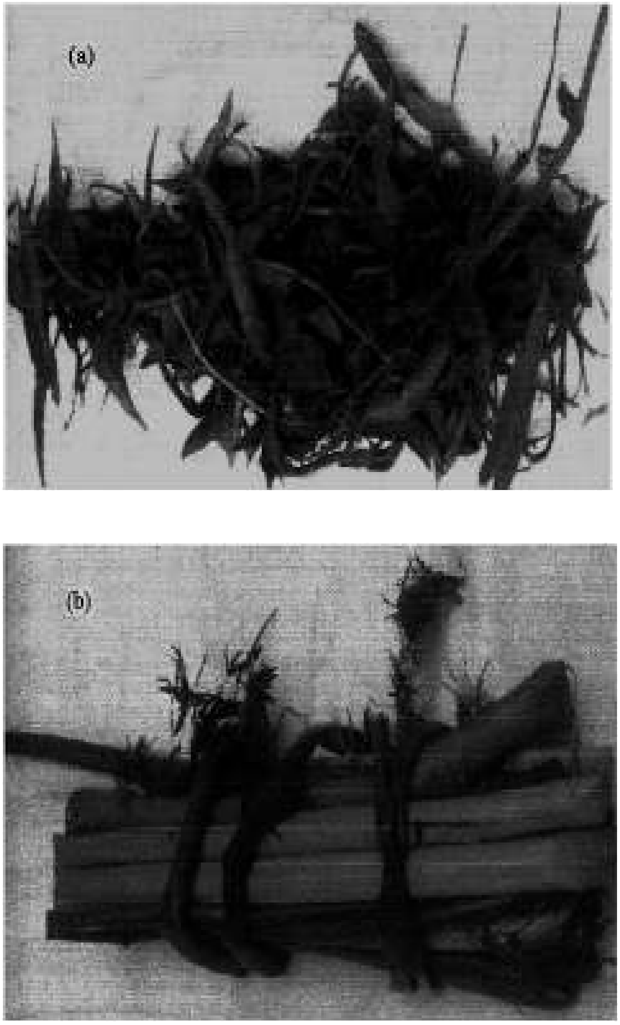

Fig. 2. *Images of submerged plants (a) Phylantus amarus and (b) Cyprus specie*

Analysis

Determination of water-borne Pb^{2+}

Water samples were analysed for Pb^{2+} immediately after sampling, using BUCK Scientific 210 VGP atomic absorption spectrophotometer (AAS). Suspended particles and plant materials were filtered off from all water samples prior to measurements. Standard Pb^{2+} solutions were prepared and run at the same time as the samples.

Determination of Pb^{2+} in submerged plants

The oven-dried plant samples were charred for 2 hours using hot plate. The charred sample (1g) was muffled at 750 °C (12 hours) and ashed with aid of $Mg(NO_3)_2$. The resulting ash was cooled in a desiccator and then weighed. The process of heating (this time for 8 hours) and cooling was repeated until constant weight. The white ash formed was dissolved in 10 % nitric acid, shaken for 15 minutes and topped to 50 ml with 1 % nitric acid. The resulting suspension was allowed to stand for 40 minutes followed by filtration. The filtrate was analysed for Pb^{2+} using BUCK Scientific 210 VGP atomic absorption spectrophotometry.

Adsorption experiments

The removal of Pb^{2+} by the leaf powders was evaluated using batch flasks containing synthetic adsorbate solutions (5 and 20 mg/L). Adsorption experiments were carried out within 0 and 120 min. The suspension of adsorbent in the adsorbate solution was stirred at 140 rpm to avoid mass incongruity. The residual adsorbate was then filtered and the amount of Pb^{2+} in the filtrate was measured on AAS. The amount of Pb^{2+} adsorbed at equilibrium was calculated using Eq (1).

$$q = \frac{(C_o - C_t)}{W} \text{ x } V \qquad (1)$$

Where C_o and C_t (mg/L) are the concentrations of Pb^{2+} determined by AAS before and after adsorption, V is the volume (L) of adsorbate solution, W is the mass (g) of bioadsorbent and q is the amount of Pb^{2+} adsorbed (mg/g).

2.2.3.1 Effect of operating variables

The influence of adsorbent dose (0.1 and 1 g) for the removal of Pb^{2+} from 25 ml of 20 mg/L Pb^{2+} solution was studied at 30 °C. pH was fixed at 4. The mixture was shaken for 60 min at 140 rpm.

The effect of pH was studied between pH 2 and pH 5, at constant adsorbent concentration (0.1 g/L) and initial lead concentration (20 mg/L) while the effect of lead concentration was studied at initial concentrations of 5 and 20 mg/l.

After adsorption experiments, suspensions were filtered through Whatman No. 42 filter paper. The filtrates were run on AAS and Pb^{2+} concentrations recorded.

RESULTS AND DISCUSSION

Pb^{+2} levels in water and submerged plant

The levels of Pb^{2+} in the water utilised for the irrigation of five different locations of the Thomas agricultural sites (A-E) were found to be 1.167, 1.833, 1.667, 2.167 mg/L, respectively which shows that the source of lead is unambiguously the irrigation water which can lead to unacceptable levels in the soil. The present concentrations of lead in the irrigation water are higher than the maximum allowed levels (0.01 mg/l) for water utility (WHO, 2006).

The levels of lead in the submerged plants studied are as follows: *Phylantus amarus*, 2.17 ± 0.5 mg/Kg; *Cyperus rotundus*, 1.33 ± 0.5 mg/Kg; *Water hyacinth*, 1.67 ± 0.9 mg/Kg; *Echinocloa colona*, 1.17 ± 0.9 mg/Kg and *Typha*, 9.66 ± 0.9 mg/Kg. These levels of lead are obviously due to long-term accumulation. A priori, the shoots of submerged plants have the potential for uptake and accumulation of heavy metals (Fritioff, 2006). Among these plants, *Typha* has the highest bioaccumulation of lead. Since these submerged plants can accumulate much more than 0.01 mg Pb^{2+}/Kg the irrigation water is not suitable for the production of edible plants (Kachenko, 2006).

Kinetics of Pb^{+2} adsorption over *Tridax procumbens*

To appropriately evaluate the possibility of removal of Pb^{2+} over leaf powder of *Tridax procumbens*, synthetic solutions of this contaminant were used, since these do not contain interfering substances. Adsorbent mass was varied between 0.1 and 1 g. At 5 mg/L initial concentrations, the highest lead removal (4.88 mg/g) was obtained using 0.1 g leaf power. The adsorption was found to decrease as pH is lowered from 4 through 2. At pH 5 there was insignificant increase in the amount of Pb^{2+} adsorbed probably due to precipitation. Sekar *et al.* (2004) reported that at pH 2-5 lead ions can precipitate out of solution. When temperature was varied from room temperature (30 °C) to 40 °C the amount of Pb^{2+} adsorbed reduced drastically. Therefore, further experiments were carried out using 0.1 g of the adsorbent dose, and at 30 °C and pH 4.

The adsorption of Pb^{2+} fitted well into the pseudo second order rate model expressed in the linearised form shown in Eq. (2).

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (2)$$

Where $h = 2k_2 q_e$. k_2 is the pseudo-second order rate constant of adsorption, q_e and q_t are the amounts of Pb^{2+} ions (mg/g) on the adsorbent at equilibrium and at time t. A plot of t/q_t against t consistently fitted into the pseudo-second order equation while in contrast, poorer agreement ($R^2 = 0.985$) was obtained when Langmuir adsorption isotherm was used.

Table 1: Pseudo-second order adsorption rate constants of Pb^{2+} at different initial concentrations over of leaf powder of *Tridax procumbens*. Adsorbent concentration = 0.1 g/L; temperature = 30 °C; pH 4.

$[Pb^{2+}]$ (mg/L)	k (g/mg min)	q_e (mg/g)	R^2	h (mg/g min)	Experimental q_e (mg/g)
5	61.89	1.21	0.998	90.91	1.21
20	1.81	4.90	0.994	43.47	4.88

CONCLUSION

Some insight could be gained from the present study of lead in Thomas dam irrigation site. First, the presence of high lead contents in the submerged plants as compared with the irrigation water is an indication of long term accumulation of this contaminant. As most submerged plants readily uptake lead into their tissues it may be inferred that rice production using this irrigation water should be discouraged. Measures should be taken to reduce the contamination of the irrigation water so as to avoid its accumulation in the soil. Finally, the effectiveness of *Tridax procumbens* for the sorption such water-borne lead ions has been successfully demonstrated.

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